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Rapid eclogitisation of the Dabie–Sulu UHP terrane: Constraints from Lu–Hf garnet geochronology

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ABSTRACT

The Qinling–Dabie–Sulu orogenic belt in eastern China is one of the largest ultrahigh-pressure (UHP) terranes worldwide. Mineral Sm–Nd- and zircon U–Pb dating has been widely used to reveal the metamorphic history of this collisional orogen. However, the exact timing of the UHP metamorphic event(s) remains controversial and ages ranging from 245 Ma to 220 Ma have been suggested. We present high precision garnet–cpx Lu–Hf ages for six eclogites from the Dabie and Sulu areas. All ages fall in a narrow range between 219.6 and 224.4 Ma. Five samples define a mean age of 223.0 ± 0.9 Ma and one sample yields a slightly younger age of 219.6 ± 1.4 Ma. This very tight age range is particularly remarkable considering the large regional distribution of sample localities (on the order of 100 km at the time of UHP metamorphism) and the wide variety of garnet and eclogite chemical compositions represented. Two samples yield Sm–Nd ages that are indistinguishable from their Lu–Hf ages, albeit with larger uncertainties.

The identical ages of eclogites from both the Dabie and the Sulu region emphasize their close genetic relationship and similar metamorphic histories. The Lu–Hf results appear to date a punctuated event of garnet growth. Alternatively, the Lu–Hf garnet ages may represent the onset of rapid, contemporaneous uplift and subsequent cooling. However, trace element zoning of Lu and Hf is still preserved in garnet porphyroblasts, even in those with a homogeneous major element distribution. Thus, complete re-equilibration of the Lu–Hf system during peak-temperature conditions probably did not occur. The garnet forming event can be placed toward the final stage of the UHP metamorphism, in agreement with some published U–Pb zircon ages. A possible trigger for this short-lived and widespread mineral growth episode may have been a fluid that became available at that stage of the metamorphic history. Although HREE-depleted patterns of older zircon grains may indicate the presence of an older generation of garnet, complete eclogitisation may have been inhibited during the major part of the prograde P–T path due to dry conditions during most of the UHP metamorphism. The uniform Lu–Hf (and Sm–Nd) ages of all investigated Dabie and Sulu eclogites suggest that garnet growth and thus possibly fluid availability were limited to a short time interval over a remarkably large regional scale.

1. Introduction

The collision between the Sino-Korean craton and the Yangtze block during the Triassic formed one of the most extensive ultrahigh-pressure metamorphic belts worldwide. Metamorphic rocks with minerals indicating extremely high-pressure conditions are exposed in the southern and eastern parts of the Qinling–Dabie–Sulu collision zone (Fig. 1A). Coesite and microdiamond have been found as inclusions in garnet and other high-pressure (HP) minerals in eclogites and country rocks, indicating deep subduction of continental material to mantle depth (e.g. Okay et al., 1989; Shutong et al., 1992). The Dabie and Sulu UHP terranes at the eastern margin of the belt contain large outcrops of HP and UHP rocks. The Sulu UHP terrane is offset by 500 km to the NE along the Tanlu Fault.

On the basis of petrographic observations, the metamorphic events that formed the Dabie–Sulu UHP terrane can be divided into three distinct stages (Cong et al., 1994; Ernst and Liou, 1999; Zheng et al., 2005): (1) a peak ultrahigh-pressure eclogite facies imprint in the coesite/diamond stability field at temperatures of 800–700 °C and pressures >2.8 GPa; (2) an episode of high-pressure quartz-eclogite

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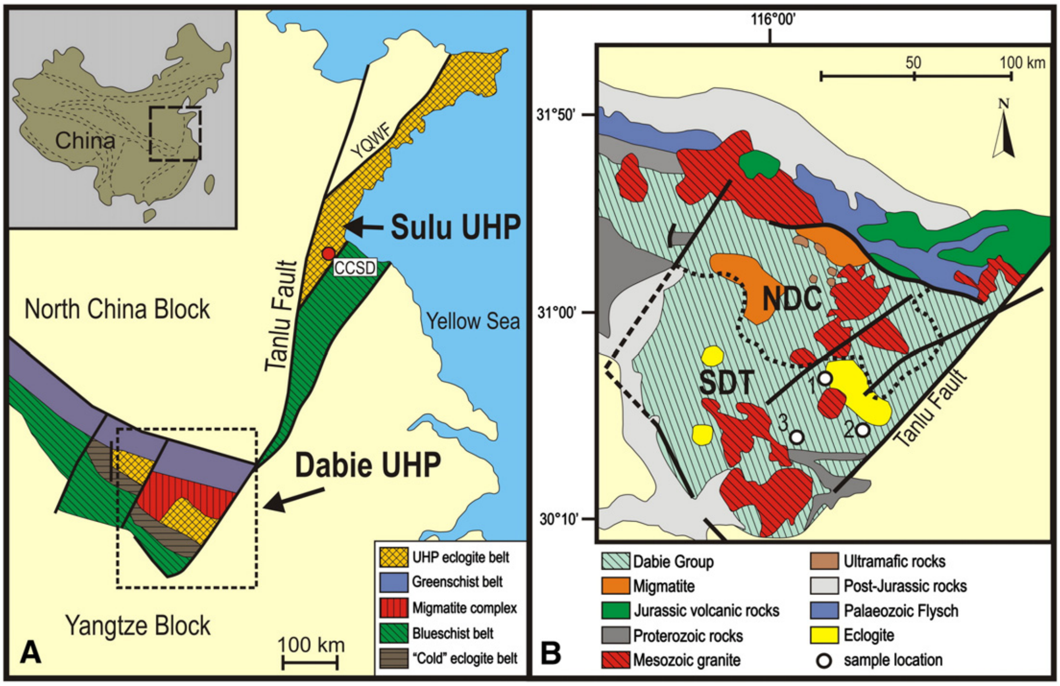

Fig. 1. A: Overview of the Dabie–Sulu terrane (with small inset showing outlines of China; CCSD = Chinese Continental Scientific Drilling, YQWF = Yantai–Qingdao–Wulian–Fault), and B: Detailed map of the Dabie terrane with sample localities (1 = Bixiling, 2 = Shima, 3 = Lidu; NDC = North Dabie Complex, SDT = South Dabie Terrane).

facies conditions at temperatures of 750–600 °C and pressures of 2.4–1.2 GPa; and (3) a retrograde amphibolite-facies overprint with replacement of omphacite by symplectites of amphibole + plagioclase at P–T conditions of 600–450 °C and 1.0–0.6 GPa.

The timing of peak metamorphism and the collision between the Sino-Korean craton and the Yangtze block are of key importance for understanding the geodynamic evolution of the Dabie and Sulu terranes. On the basis of Sm–Nd ages of eclogite minerals, the time interval between 240 and 200 Ma for the (U)HP events was proposed (Li et al., 1993). A Triassic collision was supported by many subsequent studies by Sm–Nd chronometry on garnet-bearing, (mostly) high-pressure rocks and U–Pb geochronology of zircon and other accessory minerals. However, all these studies combined provide a wide range of ages for the metamorphism and the timing of HP metamorphism is still poorly resolved. For example, an Early Triassic Sm–Nd age of 246 ± 8 Ma was obtained for eclogites exposed at Wumiao (Okay et al., 1993), but eclogites from the Bixiling Complex, the largest coesite-bearing mafic–ultramafic body in the Dabie Mountains, yielded significantly younger Sm–Nd ages of 210 ± 9 Ma to 218 ± 4 Ma (Chavagnac and Jahn, 1996). Late Triassic metamorphism is also indicated by several other published Sm–Nd ages (Li et al., 2000; Jahn et al., 2003; Li et al., 2004; Xie et al., 2004). Zircon U–Pb ages from various mafic and ultramafic rocks have been interpreted to indicate a Triassic collision event between 210 Ma and 240 Ma (Ames et al., 1993; Ames et al., 1996; Rowley et al., 1997; Hacker et al., 1998; Chavagnac et al., 2001; Ayers et al., 2002; Faure et al., 2003; Li et al., 2003, 2004; Yang et al., 2003; Zhang et al., 2005). Some authors have recently proposed an early Triassic (>240 Ma) UHP event on the basis of U–Pb zircon ages (Hacker et al., 2006; Liu et al., 2006a).

The retrograde history and uplift of the Dabie UHP rocks have been constrained by applying either thermochronological approaches, including Rb–Sr or $^{40}Ar/^{39}Ar$ on phengite (Eide et al., 1994; Chavagnac and Jahn, 1996), or by U–Pb dating of retrograde amphibolite-facies zircon (Hacker et al., 2006; Liu et al., 2006b, 2008). According to these results, cooling occurred mainly between 220 and 200 Ma, with uplift rates of about 3–10 mm/year.

In this study, the Lu–Hf system was used to date three eclogites from the Dabie Mountains at Bixiling, Lidu and Shima, as well as three subsurface eclogite samples from the Sulu terrane that were obtained during the Chinese Continental Scientific Drilling Program (CCSD). In addition, Sm–Nd dating was applied to two of the six eclogites that were dated with Lu–Hf. Lutetium–Hf geochronology has been widely used to date garnet-bearing mineral assemblages, and can reveal the timing of HP metamorphism or cooling in eclogites, eclogite facies rocks, and granulites (e.g. Duchêne et al., 1997; Scherer et al., 1997, 2000, 2003; Blichert-Toft and Frei, 2001; Lapen et al., 2003; Anczkiewicz et al., 2007; Kylander-Clark et al., 2007; Lagos et al., 2007). It has several advantages over the Sm–Nd system. In contrast to Sm–Nd, the Lu–Hf system may preferentially date initial garnet growth because Lu is commonly enriched in garnet cores (Lapen et al., 2003; Skora et al., 2006). Thus differences in Sm–Nd and Lu–Hf ages may occur if garnet porphyroblasts grew continuously over long time intervals or in two or more episodes widely spaced in time (Lapen et al., 2003; Anczkiewicz et al., 2007). The closure temperature (T_C) of the Lu–Hf system in garnet seems to be higher than that of the Sm–Nd system (Scherer et al., 2000). An advantage of applying garnet geochronology to date metamorphic events is that petrology and mineral chemistry can be used to link the garnet growth history with the P–T evolution of the host rocks. In contrast, accessory phases like zircon are often difficult to tie to specific metamorphic conditions or events (e.g. Whitehouse and Platt, 2003). One aim of this study was to test the suitability of the Lu–Hf system to date high-pressure events by applying it to one of the world's most intensely studied high-pressure terranes and interpreting it in light of existing Sm–Nd and U–Pb zircon data. The main goal was to compare the timing of (U)HP metamorphism (i.e., garnet growth) within and between the Dabie and Sulu UHP terranes to contribute to a better understanding of the geodynamic history of the eastern part of this large orogen.

2. Geological setting and sample description

The Dabie and Sulu UHP terranes are located at the eastern part of the E–W trending Qinling–Dabie–Sulu orogenic belt, which forms the collision zone between the Sino-Korean craton (explicitly the North China Block part of the craton) to the north and the Yangtze block to the south (Fig. 1A), and preserves a record of late mid-Proterozoic to

Cenozoic tectonism in Central China (Ratschbacher et al., 2003). High- and ultrahigh-pressure rock assemblages can be found in the Dabie–Sulu segment of the belt (and also the Tongbai and Hong'an segments further west), which comprise coesite- and quartz-eclogite. For detailed descriptions of the tectonic evolution and lithologies see e.g., Wang et al. (1990), and Ratschbacher et al. (2003).

The Dabie terrane can be divided into four major units (Liou et al., 1995): the North Huaiyung Flysch Belt, the North Dabie Complex (NDC), the South Dabie Collision Terrane (SDT), and the Susong Metamorphic Belt. The NDC comprises orthogneisses, migmatites, metasediments, amphibolites, and ultramafic rocks (Okay et al., 1993; Zhang et al., 1996). The NDC was subjected to intense deformation associated with the intrusion of granite bodies during the Cretaceous and has been interpreted as a thermally overprinted subduction complex (Wang and Liou, 1991; Okay et al., 1993; Maruyama et al., 1994). The SDT consists mainly of quartzofeldspathic gneisses and eclogites. Marbles, ultramafic rocks, and jadeite quartzites occur as lenses, blocks, and layers interbedded with the gneisses. Inclusions of coesite and diamond have been found in eclogite minerals (garnet, cpx, kyanite; Okay et al., 1989). Pseudomorphs after coesite and relict high P/T metamorphic assemblages have also been found in gneisses associated with the eclogites, indicating that they also underwent UHP metamorphism (Wang and Liou, 1991; Schertl and Okay, 1994; Cong et al., 1995). The SDT can be divided into a northern "hot" eclogite zone, characterized by coesite-bearing eclogites and a marble-eclogite association, and a southern "cold" eclogite zone, characterized by sodic amphibole-bearing quartz-eclogites (Okay et al., 1993). Despite this subdivision based on petrology, the peak metamorphism for both parts of the SDT is thought to be contemporaneous between 210 and 230 Ma (Ames et al., 1993; Li et al., 1993; Franz et al., 2001).

The Sulu UHP terrane is the northeastern extension of the Qinling–Dabie–Sulu orogenic belt and is offset by ~500 km along the Tanlu Fault. It consists mainly of HP and UHP eclogitic rocks in the central part, flanked by blueschist- to amphibolite-facies rocks to the south, and an amphibolite–granulite–migmatite zone to the north, separated by the Yantai–Qingdao–Wulian–Fault (YQWF; Hirajima and Nakamura, 2003).

The three eclogites from the SDT dated in the present study were collected from (1) the Bixiling Complex (sample DB05), the largest coesite-bearing eclogitic body in Dabie–Shan (described in detail by Chavagnac and Jahn, 1996, and Liou et al., 1995), (2) an eclogite outcrop near the village of Shima (DB63), and (3) an outcrop near the village of Lidu (DB44) (Fig. 1B). They are all coarse grained coesite-bearing eclogites mainly consisting of garnet + omphacite with rutile as an accessory phase (1–3%). Zircon is present as minute inclusions in garnet and omphacite. Minor amphibole forms symplectites around omphacite grains (e.g., in sample DB44). Detailed descriptions of the Dabie samples can be found in Xiao et al. (2002). Sample DB05 is a "fresh eclogite" from the central part of the Bixiling complex with no signs of retrogression. Sample DB63 of the Shima area is strongly foliated and exhibits garnet-rich layers interbedded with omphacite-rich layers, and retrogressed domains are rare. Whereas the samples DB05 and DB63 originate from the "hot eclogites" of the coesite eclogite zone in the SDT, sample DB44 represents a "cold eclogite" from the quartz-eclogite zone described by Okay et al. (1993). The three different eclogite localities from the SDT that are sampled by this study are ~40 km apart from each other.

The three samples from the Sulu orogen (PH04, PH10, and PH20) are eclogites from the main drill hole of the CCSD near Donghai (location of the drill hole is marked "CCSD" in Fig. 1A). They were collected from depths of 312, 1066, and 1993 m, respectively, and are identical to samples MH03, MH16, and MH28 in Xiao et al. (2006).

3. Analytical methods

Rock samples were processed in a jaw crusher and sieved. From the 250–355 μm sieve fraction, 0.1 to 1 g of garnet and clinopyroxene were handpicked under a binocular microscope, excluding grains having visible inclusions like rutile and zircon. Particularly zircon, if it is inherited from previous high temperature events, could bias the ages obtained by the mineral isochrons due to its high Hf-content and incomplete re-equilibration with the rock matrix during metamorphism (Scherer et al., 2000). To selectively dissolve the garnet and clinopyroxene fractions while leaving the Hf-bearing zircon and rutile largely intact, they were digested in closed Teflon® vials on a 120 °C hotplate rather than in high-pressure Parr® bombs (Lagos et al., 2007; Scherer et al., submitted for publication). After rinsing with Milli-Q H_2O, mineral separates were spiked with a mixed ^{176}Lu–^{180}Hf tracer for Lu and Hf concentration determinations, and then digested as follows: The minerals were decomposed in HF–HNO_3–$HClO_4$ and then 10 M HCl, drying down at high temperature (fuming $HClO_4$) between steps (Lagos et al., 2007). The digestion procedure was repeated once if necessary to achieve clear solutions in HCl. Separation of Lu and Hf was achieved on an ion-exchange column containing Eichrom Ln-Spec resin (Münker et al., 2001). The Hf fraction of all garnet separates was passed through an additional cation-exchange column (column A of Patchett and Tatsumoto, 1980) to remove any remaining Yb and Lu. Lutetium and Hf isotope ratios were measured on a Finnigan Neptune MC-ICPMS equipped with a Cetac ARIDUS™ sample introduction system at the University of Frankfurt. This instrumental setup ensured high sensitivity, enabling the precise measurement of Hf isotope compositions of samples having as little as 10 ng of Hf at a signal intensity of ~100 mV of ^{176}Hf for a 10 ppb Hf solution.

Because only 50–80% of the Yb were separated from Lu with the purification technique employed here, a correction was necessary for the interference of ^{176}Yb on ^{176}Lu (Blichert-Toft et al., 1997). The Yb interference was monitored by measuring two interference-free Yb isotopes (^{173}Yb and ^{171}Yb). Their ratio was used to apply an instrumental mass bias correction to measured $^{176}Lu/^{175}Lu$ values, assuming a $^{173}Yb/^{171}Yb$ of 1.129197 and the exponential law (Vervoort et al., 2004). This mass bias correction was also applied to the $^{176}Yb/^{171}Yb$ used for correcting the ^{176}Yb interference on ^{176}Lu. In-run statistics for the measured and corrected $^{176}Lu/^{175}Lu$ range from 0.006 to 0.01% 2 s.e. Mass bias on the Hf isotope ratios was corrected using $^{179}Hf/^{177}Hf = 0.7325$ and the exponential law. The Hf fractions were virtually free of any Yb and Lu, but contained various amounts of Ta and W. All isobaric interferences on Hf isotopes were monitored and corrected using the mass bias corrected $^{173}Yb/^{176}Yb$, $^{175}Lu/^{176}Yb$, $^{180}Ta/^{181}Ta$, and $^{183}W/^{180}W$ values.

During the course of this study, the Lu standard yielded $^{176}Lu/^{175}Lu = 0.026553 \pm 46$ ($2\sigma \approx 0.18\%$, $n = 23$) and the Hf Standard JMC-475 yielded $^{176}Hf/^{177}Hf = 0.282151 \pm 31$ ($2\sigma = 1.1\varepsilon$, $n = 97$, including analyses of 100, 50, 20, and 10 ppb standard solutions). In-run analytical uncertainty for $^{176}Hf/^{177}Hf$ is $\sim 0.3\varepsilon$. For the calculation of the mineral isochrons the ISOPLOT program (Ludwig, 2007) was used with a $\lambda^{176}Lu = 1.865 \times 10^{-11}\ a^{-1}$ (Scherer et al., 2001). For samples with in-run precisions (2σ errors) on $^{176}Hf/^{177}Hf$ below 1ε, uncertainties on $^{176}Hf/^{177}Hf$ were assumed to be 1.1ε (2σ) for the calculation of the isochron-ages, based on the long term reproducibility of the Hf-standard. Uncertainties on $^{176}Lu/^{177}Hf$ were propagated from the reproducibility of the Lu standard and the uncertainty in the spike calibration (0.15%), and multiplied by an error magnification factor that depends on the measured $^{176}Lu/^{175}Lu$. Resulting uncertainties for the $^{176}Lu/^{177}Hf$ values are between 0.25% and 0.35%. Repeated blank measurements yielded < 15 pg for both Lu and Hf.

The Sm–Nd analyses were performed on the same instrumental set up as for the Lu–Hf analyses. For each eclogite sample, approximately 100 mg of garnet, clinopyroxene and bulk rock were used and a mixed ^{150}Nd–^{149}Sm spike was added prior to dissolution. Samarium and Nd were separated in a 2-column ion-exchange purification procedure. A cation-exchange resin (AG1-50Wx8) was used on the first column to separate the bulk REEs from the matrix. On a second column, filled with Eichrom Ln-Spec resin, Sm and Nd were separated from the other

Table 1
Bulk rock major (in wt.%) and trace element (in ppm) compositions of (U)HP eclogites

	DB05	DB44	DB63	PH04	PH10	PH20
(wt.%)						
SiO_2	45.6	51.3	43.5	48.6	48.2	47.4
TiO_2	1.46	1.29	2.07	1.93	0.77	1.98
Al_2O_3	15.6	14.9	16.2	18.2	17.4	15.1
Cr_2O_3	0.03	0.04	0.02	0.02	0.06	0.04
FeO	16.4	9.43	13.4	11.1	10.1	13.8
MgO	7.47	7.09	5.58	6.33	9.17	7.74
CaO	10.7	10.4	16.7	9.18	9.90	10.8
MnO	0.22	0.22	0.26	0.25	0.21	0.22
NiO	0.03	0.25	0.01	0.01	0.04	0.02
Na_2O	2.36	4.82	2.12	2.58	2.80	2.40
K_2O	0.06	0.11	0.03	1.27	1.16	0.32
P_2O_5	0.07	0.18	0.15	0.54	0.21	0.12
(ppm)						
Sr	107	97.8	125	143	60.4	244
Y	10.1	14.7	29.3	11.3	19.4	14.4
Zr	23.5	125	41.4	33.9	71.5	52.3
Nb	0.75	3.74	7.23	0.75	1.67	1.31
La	10.0	5.48	11.9	4.51	21.0	1.88
Ce	24.6	11.3	23.2	9.41	40.5	2.71
Pr	3.60	1.458	2.88	1.40	5.01	0.555
Nd	16.3	6.26	11.6	7.23	20.1	3.64
Sm	3.10	1.43	3.31	2.13	3.84	1.92
Eu	1.11	0.636	1.37	1.33	1.39	1.16
Gd	1.77	1.50	3.82	2.04	2.76	2.16
Tb	0.325	0.431	0.881	0.371	0.530	0.441
Dy	2.02	2.94	5.37	2.31	3.53	2.74
Ho	0.457	0.645	1.12	0.519	0.856	0.632
Er	1.150	1.56	2.52	1.30	2.28	1.61
Tm	0.161	0.208	0.301	0.180	0.341	0.228
Yb	1.021	1.37	1.75	1.18	2.35	1.49
Lu	0.156	0.216	0.249	0.187	0.380	0.231
Hf	0.748	3.13	1.20	4.20	1.32	1.14
Ta	0.04	0.18	0.36	0.06	0.07	0.06
Pb	2.93	3.20	5.16	3.25	5.18	4.21
Th	0.535	0.458	1.13	0.336	2.17	0.039
U	0.100	0.144	0.727	0.231	0.304	0.044

REE (Pin and Zalduegui, 1997). The mass bias of Nd isotope ratios was corrected using $^{146}Nd/^{144}Nd = 0.7219$ and the exponential law. For Sm, $^{147}Sm/^{152}Sm$ was used for mass bias correction. Multiple analyses of the AMES Nd standard yielded $^{143}Nd/^{144}Nd = 0.511912 \pm 33$ ($2\sigma \approx 0.7\varepsilon$, $n = 8$). During Nd analyses, ^{147}Sm was monitored to correct for possible isobaric interferences on ^{144}Nd, ^{148}Nd, and ^{150}Nd. However, the monitored ^{147}Sm and ^{149}Sm in the Nd fraction were at the background level and interference corrections were thus applied using the natural (rather than the spiked) $^{144}Sm/^{147}Sm$, $^{150}Sm/^{147}Sm$ and $^{148}Sm/^{147}Sm$ values. Varying amounts of Gd were present in the Sm fraction and corrected for using the mass bias corrected $^{155}Gd/^{152}Gd$ and $^{155}Gd/^{154}Gd$ ratios. The 2 S.D. error for $^{143}Nd/^{144}Nd$ of replicate AMES standard measurements was used for the calculations of the Sm–Nd isochrons. Errors on the $^{147}Sm/^{144}Nd$ ratios were estimated to be 0.12% on the basis of the reproducibility of Sm- and Nd isotope ratios. All errors on the ages of the Model 1 Lu–Hf and Sm–Nd isochrons in this study are reported at the 2σ level as calculated by the ISOPLOT program.

The major element composition of the bulk rocks was determined using a JEOL Superprobe JXA-8900 on fused glasses (with run parameters of 15 keV, 20 nA, and 3 µm spot size). The same setup was used for the major element analyses of garnets in thin sections. The fused glasses were produced by rapid heating (<30 s) of ~100 mg of sample (without using a flux) on an Ir-strip, followed by rapid quenching. These glass pellets were also used for trace element analyses of the bulk rocks, which were performed by Laser Ablation (213 nm Nd-YAG UV-Laser, Merchantec) coupled with a Finnigan Element-2 single-collector ICPMS. Laser spot sizes ranged from 90–120 µm and a laser energy between 1.5 and 4.0 J/cm² was used. The

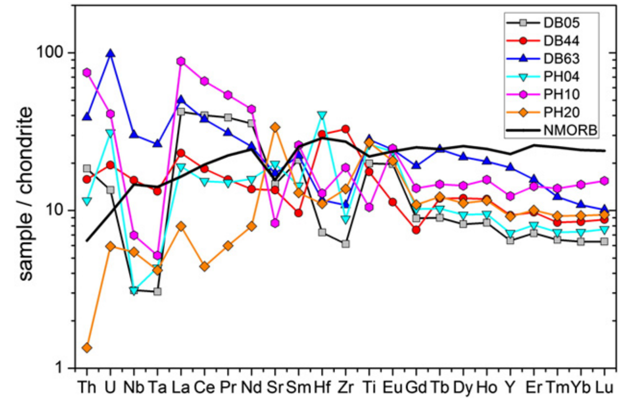

Fig. 2. Chondrite-normalized trace element patterns of the bulk eclogites (normalized to C1 of McDonough and Sun, 1995). Black line denotes chondrite-normalized NMORB for reference.

BIR1-G basalt glass standard was used for external and the ^{29}Si of the samples for internal calibration of trace element analyses. The same LA-ICPMS setup was used for the rim to rim line scans performed on single garnet grains in thick sections. Scans were continuous transect lines across approximately center-cut garnet grains with a laser spot size of 40–60 µm.

4. Results

4.1. Bulk rock composition

The major and trace element compositions of the bulk rocks are given in Table 1. SiO_2 contents range from 45.6 to 51.3 wt.%. The results agree with analyses of the same samples by Xiao (2000). In a TAS-diagram (Fig. S1 supplementary online material, s.o.m.) 5 samples plot in the basalt field while sample DB63 plots in the picro-basalt field. Samples from the Dabie terrane (DB) have lower K_2O contents (0.03–0.11 wt.%) than samples from the Sulu terrane (PH, 0.32–1.13 wt.%). Two of the three latter samples have $K_2O > 1$ wt.%. In the AFM diagram (Fig. S2 s.o.m.) most samples follow a tholeiitic differentiation trend (also supported by a cation plot, s.o.m.).

Fig. 2 shows the chondrite-normalized trace element patterns of the bulk rocks. All samples display a more or less evolved positive Eu anomaly and relatively flat REE patterns with only slightly elevated LREE. Samples PH04 and PH20 have a positive, while all other samples have a negative Sr anomaly or a rather flat pattern. All samples show pronounced negative Nb–Ta anomalies and positive and negative Ti, Hf, and Zr anomalies. The compositional variety observed in all 6 eclogite samples can be attributed to both igneous (heterogeneous

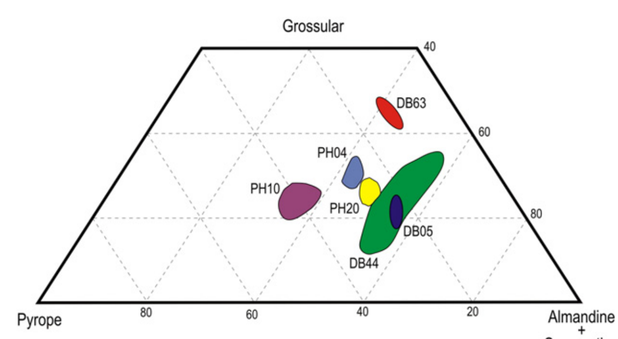

Fig. 3. Ternary plot of the cation percent of Mg (pyrope), Ca (grossular) and Fe+Mn (almandine+spessartine) in eclogite garnet porphyroblasts.

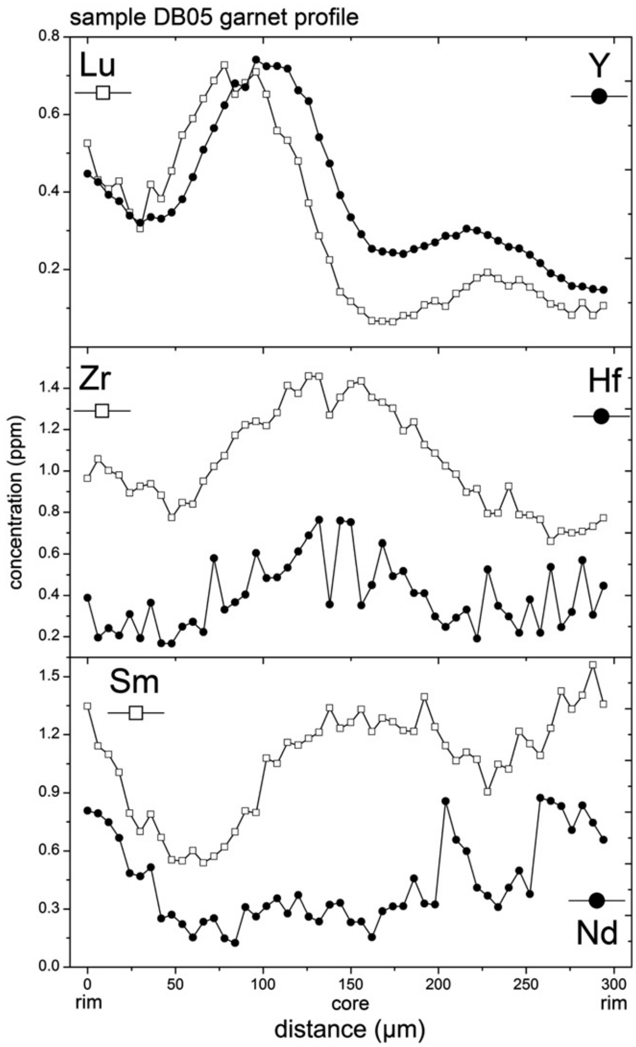

Fig. 4. Lu, Y, Hf, and Zr profiles of garnets in sample DB05 performed by LA-ICP-MS.

protoliths) and metamorphic processes. Recently it was suggested that the eclogite protoliths originated from a basaltic magma that formed in a continental setting (Tang et al., 2007).

4.2. Mineral composition

The major element composition of the garnets in the investigated eclogites is shown in Fig. 3 (and Table S-1, s.o.m.). There are large variations between garnets of different samples. Within each sample, however, most garnet grains are homogeneous. Clinopyroxenes in all rocks are omphacites having jadeite components ranging from 35 to 60% and a minor acmite component. Compositional maps of two garnet grains (samples PH20 and DB44) for the elements Mg, Fe, Ca and Mn are shown in the supplementary online material (Fig. S-3). The grain in sample PH20 is a typical garnet, similar to all analysed samples, except for DB44, with respect to major element distribution and size. All mapped elements in this garnet are homogenously distributed and there is no compositional zoning in core and rim regions. In contrast, the garnet grains in sample DB44 are clearly zoned and show distinct core and rim regions.

To investigate the trace element distribution of the garnets, several line scans were performed across individual garnet grains with LA-ICPMS. The line scans were placed to cut from rim to rim through the center of single garnet grains from thick sections. Since it cannot be assured that the real center of the garnet was sampled, any observed zoning represents a minimum zoning of respective garnets. Fig. 4 shows a representative rim to rim scan for the elements Lu, Y, Zr, Hf, Sm, and Nd in sample DB05. Since the Hf concentrations in the garnets are mostly near the detection limit of the LA-ICPMS, its geochemical twin Zr was used as a proxy for the distribution of Hf in samples with very low concentrations. Zirconium was also used as a tracer for potential zircon inclusions. However, in the case of sample DB05, the Hf concentration was sufficient to record a meaningful profile. The scan shows the expected Lu enrichment in the garnet core region and also distinct peaks in the Y, Hf, and Zr concentrations. Interestingly, the Lu and Y peaks are offset from each other, and both peaks are offset from those of Hf and Zr. Samarium shows irregular enrichment to the right, Nd shows no marked zoning. Additional garnet profiles for Lu can be found in the supplementary online material.

4.3. Lu–Hf and Sm–Nd ages

The results of the Lu–Hf analyses are shown in Table 2 and Fig. 5. The garnet+cpx isochrons yield a tight cluster of late Triassic ages between 219.6 Ma and 224.4 Ma. The average age of all six samples is 222.4 Ma. Combining the five analytically indistinguishable samples (and excluding the youngest sample PH10) yields a pooled age of 223.0±0.9 Ma (2 s.e.).

Table 2
Lu–Hf isotope results for eclogites and their main constituents garnet and omphacite

Sample	Fraction	Lu (ppm)	Hf (ppm)	$^{176}Lu/^{177}Hf$	$^{176}Hf/^{177}Hf$	Isochron initial $^{176}Hf/^{177}Hf$	Isochron age (Ma)
DB05	cpx1	0.020	0.118	0.01402	0.282900±28	0.282843±22	223.43±0.92
	cpx2	0.020	0.118	0.02430	0.282948±35		
	grt1	0.337	0.022	2.162	0.291865±38		
	grt2	0.348	0.018	2.694	0.294101±35		
DB44	cpx	0.012	0.119	0.01483	0.282456±14	0.282394±31	224.4±1.2
	grt	1.165	0.057	2.893	0.294528±28		
DB63	cpx	0.007	0.079	0.01318	0.282490±28	0.282436±30	222.94±0.95
	grt1	0.421	0.025	2.371	0.292284±23		
	grt2	0.419	0.030	1.988	0.290734±21		
	grt3	0.419	0.025	2.374	0.292360±20		
PH04	cpx	0.014	0.128	0.01575	0.282846±11	0.282779±30	222.7±1.6
	grt1	0.367	0.052	0.9988	0.286928±40		
	grt2	0.364	0.034	1.513	0.289081±18		
PH10	cpx	0.036	0.137	0.03696	0.282673±16	0.282522±31	219.6±1.4
	grt	0.933	0.067	1.964	0.290584±11		
PH20	cpx	0.031	0.168	0.02651	0.282712±08	0.282603±31	221.4±1.2
	grt1	0.479	0.039	1.733	0.289781±20		
	grt2	0.477	0.033	2.051	0.291087±22		

The error on $^{176}Hf/^{177}Hf$ is 2σ. Errors of the isochron-ages are reported as the 2σ error from a model 1 fit of the ISOPLOT program. Isochron initials are shown with a 2σ error.

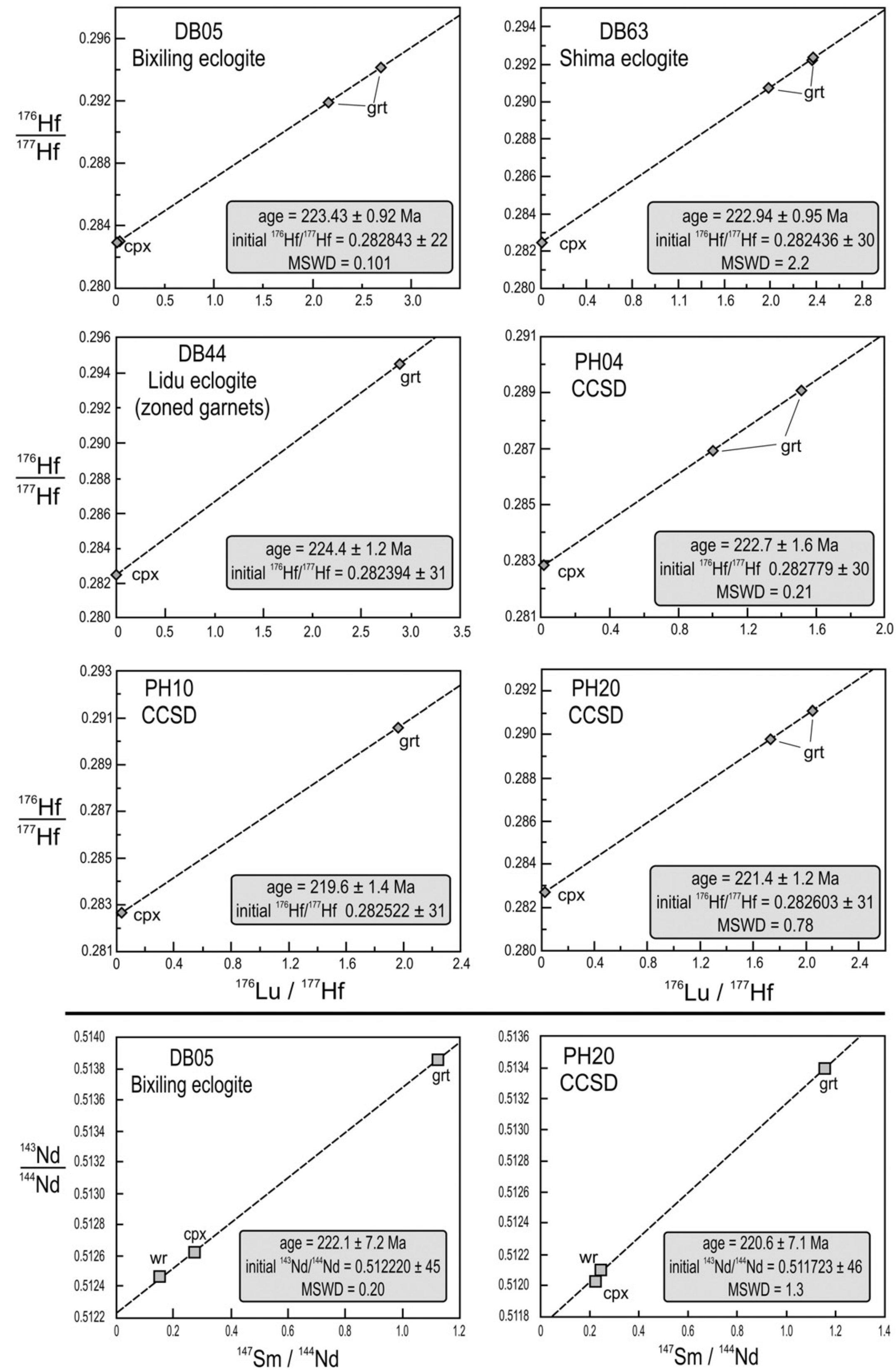

Fig. 5. Lu–Hf and Sm–Nd garnet + clinopyroxene isochrons of the Dabie and Sulu UHP eclogites. Age errors are 2σ of a model 1 fit in the ISOPLOT program. Individual errors are smaller than the size of the symbols.

All Lu–Hf ages are based on isochrons defined by garnet + omphacite, two phases that likely were in isotopic equilibrium during eclogite facies metamorphism. No bulk rock data were used for the calculations of the Lu–Hf isochrons because inherited accessory minerals, particularly unequilibrated zircon, can affect their compositions and result in spurious garnet-whole rock ages as detailed in Scherer et al. (2000). If fine bulk rock powders are dissolved, zircons cannot be excluded with the dissolution technique used in this study. Although not common in basalts, zircon is an abundant accessory mineral in eclogites from the Dabie–Sulu area and was observed in thin sections of the investigated eclogites and also as insoluble inclusions left after complete garnet dissolution. If the applied dissolution technique failed to separate zircon inclusions in garnet, this would have produced variations in the Lu–Hf systematics of different garnet separates from the same sample, which are in fact observed. However, all samples with two garnet fractions still provide well-defined isochrons with omphacite. Accordingly, if partially digested zircon inclusions produced the variability of different garnet fractions, they were probably cogenetic with the garnet. More likely, variation in Lu–Hf systematics between two garnet separates from the same sample are caused by either zoning and biased hand-picking or contamination by traces of omphacite. In the latter case, all analysed garnet fractions can be considered to lie on mixing lines between "pure" garnet and cpx that coincide with the respective isochrons. Consequently, the four isochrons that include two garnet fractions are still essentially two-point isochrons. Nevertheless, the fact that garnet separates of these samples always fit on their respective isochrons within analytical uncertainties, demonstrates the precision of the digestion method. The strongest indicator for the cogenetic nature of the garnet–omphacite assemblages is that ages of all samples are virtually identical. If cpx and garnet were not grown together in isotopic equilibrium a large scatter of ages would be expected, as the modal abundances of cpx and garnet between the analysed samples are highly variable.

The results of the Sm–Nd analyses for two eclogites (DB05 + PH20) are shown in Table 3 and Fig. 5. The garnet + clinopyroxene + whole rock isochrons provide ages of 221.1 ± 7.2 Ma and 220.6 ± 7.1 Ma which are indistinguishable from the Lu–Hf ages. Here, whole rock data were included because there seem to be no REE-rich minerals robust enough to be inherited from much older events. However, the Sm–Nd garnet–cpx ages exhibit distinctly larger uncertainties than corresponding Lu–Hf ages despite similar analytical uncertainties in the measured isotope- and parent–daughter ratios. This is due to the significantly larger spread of $^{176}Lu/^{177}Hf$ as compared to that of $^{147}Sm/^{144}Nd$ between garnet and clinopyroxene and the higher decay constant of ^{176}Lu compared to that of ^{147}Sm.

5. Discussion

5.1. Comparison of Lu–Hf ages with previously applied dating techniques

All Sm–Nd and Lu–Hf ages determined during this study of eclogites from both the Dabie and Sulu terranes range between 219.6 and 224.4 Ma. This tight age range, mainly defined by the Lu–Hf system, contrasts dramatically with the numerous results of previous Sm–Nd and U–Pb studies on different minerals from eclogites, gneisses, and other metamorphic rocks from both the Dabie and Sulu terranes (Fig. 6). Both the U–Pb ages of metamorphic zircon, monazite, titanite, and rutile, and the Sm–Nd garnet–cpx-whole rock ages display a wide range between 200 Ma and 255 Ma, as summarized in Fig. 6. This figure shows both conventional TIMS and in-situ SHRIMP and LA-ICPMS analyses. Grouping of data (e.g., pooling of U–Pb ages) and classification into metamorphic episodes provided by previous workers is not shown because classification schemes differ among individual studies. Consequently, assigning ages to separate events strongly depends on the interpretation of the data. Only zircon rims that are attributed to late amphibolite-facies metamorphism are highlighted in Fig. 6. Compared to all applied methods of previous geochronological studies, the Lu–Hf garnet–cpx ages of the present study are unique with respect to their precision and the tight age range they define. Most Lu–Hf ages of this study overlap within their analytical uncertainties, and show a narrow absolute range of only 4.8 Myr. This finding is intriguing given that the investigated rocks differ widely in their bulk (and garnet) compositions, and were regionally separated from each other by ≥ 100 km. (The actual position of the Sulu terrane relative to the Dabie terrane at the timing of the collision is not fully constrained however). The comparison of the spread given by the Lu–Hf data of this study with that of other techniques (Fig. 6) may indicate that the Lu–Hf system is particularly suitable to date UHP events, perhaps because of fewer analytical difficulties. Alternatively, it may provide the age of a specific punctuated event during eclogite facies metamorphism, while the age of other techniques is more affected by different mineral growth episodes during the metamorphic evolution of the UHP rocks.

In fact, Sm–Nd mineral isochrons of this and previous studies are characterized by larger analytical uncertainties as compared to the Lu–Hf isochrons presented here. This can be attributed to the smaller fractionation of Sm/Nd between garnet and cpx. Corresponding uncertainties for Sm–Nd ages are typically on the order of 5–10 Myr. Because most of the Sm–Nd ages for the Dabie–Sulu terrane lie between 210 and 240 Ma, many of them are analytically indistinguishable. Slightly younger Sm–Nd ages (e.g., Chavagnac and Jahn, 1996) could be explained by a lower T_C of Sm–Nd as compared to that of Lu–Hf in garnet (Scherer et al., 2000). Additionally, Lu is often highly enriched in the cores of garnets that have not been subjected to very high temperatures (Fig. 4). Thus, in contrast to Sm–Nd, Lu–Hf ages are often biased toward the time of garnet core growth (e.g., Lapen et al., 2003). However, such a systematic shift between Lu–Hf and Sm–Nd ages cannot be confirmed either by this study alone or by comparison with the average of published Sm–Nd ages of the Dabie–Sulu metamorphic rocks (Fig. 6). Rather, the identical Sm–Nd and Lu–Hf ages of our samples suggest that both isotope systems most likely date the same event.

The published U–Pb results on zircon and other accessory minerals define an even larger age range for UHP metamorphism (UHPM) in the Dabie–Sulu region (200 Ma to 255 Ma). Based on U–Pb zircon ages, at least three distinct episodes of eclogite facies metamorphism for the Dabie terrane have been defined (Liu et al., 2006a, crosshatched vertical bars in Fig. 6) at 242.1 ± 0.4 Ma (UHPM onset > 2.7 GPa), 227.2 ± 0.8 Ma (peak UHPM > 4 GPa) and 219.8 ± 0.8 Ma (quartz stability ≈ 1.8 GPa before exhumation). Multiphase mineral textures and index minerals enclosed in zircon were used to link these U–Pb ages with distinct metamorphic events (Liu et al., 2006a). However, the continuous range of zircon ages (Fig. 6) may point to continuous zircon growth over ≈40–50 Ma under variable metamorphic conditions and/or partial Pb-loss. On the basis of U–Pb zircon and Th–Pb monazite ages in combination with U–Pb and Sm–Nd data from the literature, Hacker et al. (2006) divided the history of the Dabie–Sulu terrane in two UHP stages and one retrograde stage (grey boxes in Fig. 6): (1) a "precursor" UHP event at 244–236 Ma, (2) a second UHP "main" event between 230 and 220 Ma, and (3) a terminating amphibolite-facies overprint at 220–205 Ma. In the context of these interpretations, the Lu–Hf and Sm–Nd ages of the present study appear to date a well-defined event, which coincides with the late second episode of eclogite facies (or UHP) metamorphism.

Table 3
Sm–Nd isotope results for eclogites and their main constituents garnet and omphacite

Sample	Fraction	Sm (ppm)	Nd (ppm)	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	Isochron initial $^{143}Nd/^{144}Nd$	Isochron age (Ma)
DB05	grt	0.7269	0.393	1.1227	0.513853 ± 41	0.512220 ± 45	222.1 ± 7.2
	cpx	0.5775	1.277	0.2759	0.512613 ± 21		
	wr	1.974	8.163	0.1535	0.512451 ± 08		
PH20	grt	1.751	0.926	1.1571	0.513393 ± 27	0.511723 ± 46	220.6 ± 7.1
	cpx	1.082	2.953	0.2233	0.512025 ± 24		
	wr	2.068	5.156	0.2455	0.512098 ± 07		

The error on $^{143}Nd/nnn^{144}Nd$ is 2σ. Errors of the isochron-ages are reported as the 2σ error from a model 1 fit of the ISOPLOT program. Isochron initials are shown with a 2σ error.

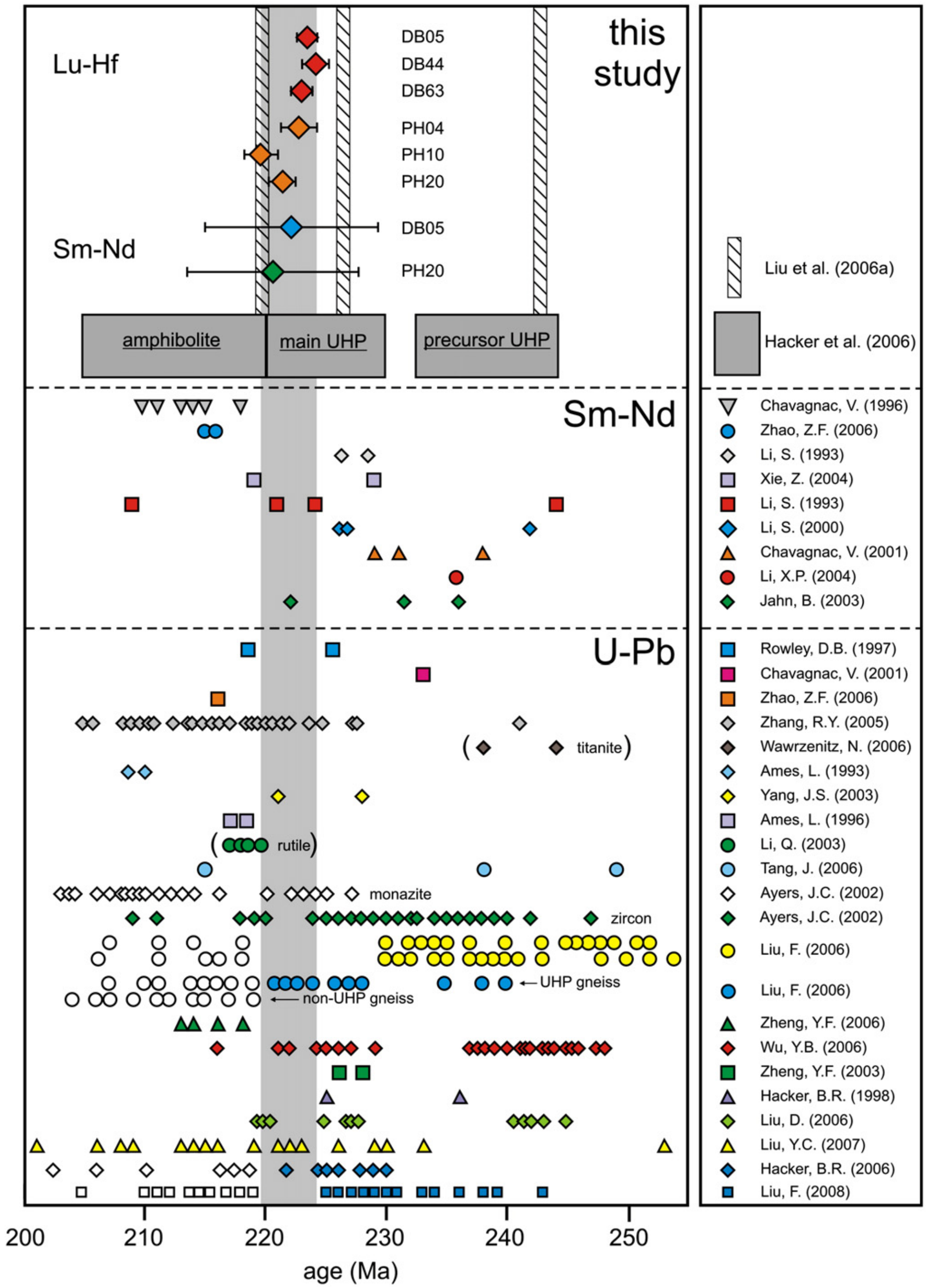

Fig. 6. Comparison of geochronological data from the literature with the results of this study. No data interpretation by the corresponding authors or pooling of data is shown, except the vertical crosshatched and horizontal bars as described in the text. U–Pb zircon ages comprise TIMS, SHRIMP, and LA-ICPMS data. Individual errors are left out for clarity. Open symbols represent zircon rims (data from Ames et al., 1993; Li et al., 1993, 2000, 2003, 2004; Ames et al., 1996; Chavagnac and Jahn, 1996; Rowley et al., 1997; Hacker et al., 1998, 2006; Chavagnac et al., 2001; Ayers et al., 2002; Jahn et al., 2003; Yang et al., 2003; Zheng et al., 2003b; Xie et al., 2004; Zhang et al., 2005; Liu et al., 2006a,b,c, 2007, 2008; Tang et al., 2006; Wawrzenitz et al., 2006; Wu et al., 2006; Zhao et al., 2006).

The agreement of the Lu–Hf and Sm–Nd ages and the tight cluster of the Lu–Hf ages can be the result of either a regional punctuated garnet growth event, or be due to re-equilibration (through re-crystallization or diffusion) of Lu, Hf, Sm and Nd and all the major elements during peak-temperature conditions followed by rapid and regionally identical uplift and cooling below the T_C of these elements. In the latter case, the cooling rate must have been fast enough to ensure that the time interval between closure of the Lu–Hf and Sm–Nd systems cannot be resolved analytically, as is the case here (i.e., Lu–Hf: 223.0 ± 0.9 Ma vs. Sm–Nd: 221.4 ± 1.5 Ma). The closure temperature of Sm–Nd in garnet has been estimated to be ca. 650 °C (Mezger et al., 1992). In contrast, the T_C of Lu–Hf in garnet is likely more than 90 °C higher than that of Sm–Nd in the same garnet (Scherer et al., 2000, using the updated decay constant of Scherer et al., 2001). If the Lu–Hf and Sm–Nd ages represent sequential cooling from above the T_C's of both systems, minimum cooling rates for PH20 and DB05 would have been ca. 9 °C/Myr at the time these systems closed.

5.2. Garnet zoning

The homogeneous major element distribution in most garnet porphyroblasts indicates that P–T–X conditions might have been rather constant during their growth or that the garnets were homogenized by diffusion during peak metamorphic conditions. Only the large euhedral, zoned garnets in sample DB44 apparently have grown under changing P–T–X conditions. This sample belongs to the so-called "cold eclogites", a different eclogite type as compared to the "hot eclogites" represented by the other samples. Temperatures for the hot eclogite zone reached 800±50 °C whereas the cold eclogite zone equilibrated at 635±40 °C (Okay et al., 1993). Most garnets however, including those with homogeneous major element compositions, have preserved trace element zoning, including Lu and Hf (Fig. 4), indicating that they have not been completely homogenized. Lutetium is commonly enriched in the cores of the studied garnet grains, which strongly indicates the preservation of growth zoning (Otamendi et al., 2002; Lapen et al., 2003; Anczkiewicz et al., 2007). Zirconium and Hf also display zoning in most garnet porphyroblasts. The preservation of apparent growth zoning in Hf, and also the presumably faster-diffusing Lu (e.g., Van Orman et al., 2002) strongly suggests that complete homogenization of Hf isotopic compositions was not achieved during the last metamorphic peak. The observed shift in the Lu+Y peaks relative to the Hf+Zr peaks is probably a consequence of asymmetrical garnet growth or heterogeneous distribution of these elements in the matrix adjacent to the growing garnet. If the Lu peak in Fig. 4 is considered to be the core of the garnet, the Sm profile shows an enrichment in the rim region, which is also expected during garnet growth (e.g., Skora et al., 2006).

Apparent partition coefficients of Lu between garnet and cpx fractions can be calculated using the available concentration data of Table 1. $D_{\mathrm{LU}}^{\mathrm{cpx/grt}}$ are between 0.01 and 0.07 and overlap with the range of partition coefficients for Lu between these two phases observed in various crustal and mantle eclogites (i.e., 0.001 to 0.2; Harte and Kirkley, 1997; Jacob and Foley, 1999; Sassi et al., 2000; Barth et al., 2002; Jahn et al., 2003; Zong et al., 2007). Hence, trace element disequilibrium between garnet and cpx, or a resetting limited to clinopyroxene only, are not indicated. As previously mentioned, important evidence for isotopic equilibrium between cpx and garnet might also be the tight range of Lu–Hf isochron-ages itself. Such a narrow range for different eclogites is rather unlikely if clinopyroxenes and garnets did not grow together or were affected by separate re-equilibration events.

5.3. Age interpretation

The high temperatures, at least those of the hot eclogites (>750 °C), may imply that both the Lu–Hf and Sm–Nd isotope systems have been open continuously during peak metamorphism, assuming closure temperatures for the Lu–Hf system in garnet between 550 and 800 °C (Scherer et al., 2000; Anczkiewicz et al., 2007). Closure temperatures vary depending on the grain size and shape (i.e., effective diffusion radius), the chemical composition of the garnet, and the cooling rate. Considering the observed chemical and morphologic differences among the investigated garnet porphyroblasts (e.g., small and homogeneous vs. large and zoned), differences in the T_C of Lu–Hf may well exceed 100 °C. The nearly identical ages of these garnets would then indicate a minimum exhumation rate of 3–5 mm/yr (assuming a retrograde thermal gradient of 5–10 °C/km for subduction zones), which is similar to the exhumation rates suggested for the Sulu UHP terrane (Liu et al., 2008). This is not particularly fast when compared to uplift rates indicated by UHP rocks from smaller geologic units like Dora Maira (Gebauer et al., 1997; Chopin and Schertl, 1999) or the Kokchetav Massif (Hermann et al., 2001; Hacker et al., 2003; Dobretsov and Shatsky, 2004). However, this model would still require rapid and simultaneous cooling of the whole Dabie UHP orogen to below the closure temperatures of the Lu–Hf and Sm–Nd, respectively.

A second way to explain the tight range of Lu–Hf (and Sm–Nd) ages might be a punctuated event of garnet growth or re-crystallization. In fact, this should result in major and trace element and isotopic re-equilibration. However, different garnet generations were not detected in the analysed garnets. In contrast, most garnet porphyroblasts preserved trace element patterns that are typical for prograde growth, that is, a distinct HREE enrichment in the garnet core regions. Accordingly, even if some retrograde re-crystallization at the garnet rims occurred, Lu–Hf ages will preferentially date the garnet cores. Therefore, the most likely explanation for the tight range of Lu–Hf ages is that they date a punctuated event of garnet growth around 223 Ma.

Since some metamorphic zircon grains in the eclogites (including those with U–Pb ages older than the Lu–Hf ages) display HREE depletion (e.g., Liu et al., 2006a,b) it is unlikely that the rocks were garnet-free before the time interval given by the Lu–Hf ages. However, new garnet growth could have been triggered on a regional scale. The phenomenon of anhydrous mafic rocks not reacting during prograde metamorphism due to kinetic inhibition is known from HP rocks, as in the case of the Bergen Arcs in Norway, where the process of eclogitisation of an anhydrous protolith can be observed in its arrested state (Austrheim and Griffin, 1985; Fountain et al., 1994). A similar situation may apply to the eclogites in the Dabie–Sulu area. As indicated by the major and trace element compositions of these eclogites, their protolith was of basaltic composition and likely anhydrous gabbro in most cases, as indicated by their positive Eu anomaly. However, whereas in the Bergen Arcs, eclogitisation is restricted to shear zones along which fluids infiltrated the anhydrous protolith and triggered the formation of the eclogite mineral assemblage (Austrheim and Griffin, 1985; Austrheim, 1986/1987; Jamtveit et al., 1990; Fountain et al., 1994), fluid infiltration in the Dabie–Sulu area must have occurred on a large regional scale. Additionally, the reaction must have gone to completion without leaving any unreacted protoliths behind. The reaction may have been triggered by a fluid, by shearing, or both after the stability field of the mineral assemblage in the protolith was significantly overstepped. In completely anhydrous rocks, such overstepping of reactions is possible (Wood and Walther, 1983; John et al., 2004), as they are diffusion controlled, which may generate a delay until a fluid becomes available that allows dissolution of metastable phases and re-precipitation of the new equilibrium phases. In the case of the eclogites of the Dabie–Sulu region, the fluid, which was most likely hydrous, must have become available instantaneously on a geologic timescale, possibly due to dehydration reactions or a change in the overall geologic setting that changed the fluid paths during subduction. In fact, Zheng et al. (2003a), proposed a short event of fluid availability for the Dabie and Sulu eclogites, according to their $\delta^{18}O$ characteristics. Shear zones similar to those described from the Bergen Arcs have not been observed in the case of the Dabie and Sulu UHP terranes. However, the small grain size of most samples and the layered structure of some of the eclogites may also indicate that the mineral reaction may have been initiated due to shearing well after the stability field of eclogite was reached. The shearing process then may have triggered rapid mineral growth, further enhanced by the release of thermal energy due to the reaction. As a result eclogites may not have formed by continuous prograde metamorphism (increasing P and T) but rather by a punctuated event.

6. Conclusions

Applying the Lu–Hf isotope system to garnet–cpx mineral pairs of the Dabie–Sulu orogen yields a very tight age range of 219.6 to 224.4 Ma with a mean age of 222.4 Ma. The Lu–Hf ages agree well with the Sm–Nd ages from the same samples, and are more precise. This close agreement of all isochron-ages can be interpreted as (1) a short garnet growth event during (or at the final stage of) UHP metamorphism, or (2) re-equilibration of Lu–Hf and Sm–Nd until or during the onset of rapid cooling and uplift. In either case, the geodynamic processes must have been relatively rapid and contemporaneous over a large regional scale. However, the preserved zoning of trace element compositions in garnets strongly indicates that the Lu–Hf isotope system has remained essentially undisturbed after garnet growth. This implies that most garnet formed within a very limited time interval at 223.0 ± 0.9 Ma as indicated by five of the six samples studied. Despite the fact that today the Dabie and Sulu terranes are offset by the Tanlu fault, the Lu–Hf results support their close genetic relationship and a contemporaneous metamorphic history of both terranes.

Intriguingly, most of the previously observed U–Pb zircon ages imply an earlier—and substantially longer—period of UHP metamorphism, or even several HP and UHP events (Hacker et al., 2006; Liu et al., 2006a, 2008). Ambient UHP conditions during zircon growth are indicated by coesite inclusions, and HREE-depleted patterns of some zircons perhaps indicate the presence of some garnet before 225 Ma. These zircons may stem from more hydrous rocks, in which the fluid availability that triggered zircon (and garnet) growth occurred earlier. However, the uniform garnet growth ages of this study imply that a major eclogitisation event occurred relatively late, near the end of the final stage of the proposed UHP metamorphic period. They further indicate that eclogitisation may generally occur during distinct and relatively short periods of fluid availability, even if the entire (U)HP event lasted much longer. The questions of whether garnet and UHP zircon grew during the same or separate events, and whether cpx and garnet re-equilibrated after zircon growth may be resolved by future studies that perform both U–Pb zircon- and Lu–Hf garnet–cpx dating on the same samples.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.epsl.2008.06.036.

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